776. *Reactions and Stability of Chabazite-like Phases. Part I. Ion-exchanged Forms of Natural Chabazite.*

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The effects of heat upon cation-exchanged forms of chabazite have been investigated by differential thermal analysis, thermogravimetry, and *X*-ray diffraction. Eleven cation-exchanged forms of a rather siliceous chabazite having a silica : alumina ratio a little above 5, and the temperature interval 20° to ~1100°, were used. The influence of the cation on thermal stability was in the order Li < Na < K < Rb < Cs, and on water retentivity in the order Li > Na > K > Rb. Bivalent ions show greater retentivity for comparable radii than do univalent ions. In several instances loss of water occurred in more than one stage.

Besides glassy products, decomposition of the parent lattice yielded quartz in a number of instances, also β-eucryptite, leucite, and the hydrogen form of chabazite.

THE synthetic mineral-type compounds grown in these laboratories [1] include a range of phases related in structure to chabazite–gmelinite minerals.[2, 3] They include a group of potassium aluminosilicates characterised by a variable alumina : silica ratio ranging from 1 : 2·3 to 1 : 4·15. Natural chabazites may also vary in their alumina : silica ratios, but on the whole are more siliceous than the potassium aluminosilicates referred to above, while in the naturally occurring crystals the cations present are sodium and calcium. Also more siliceous phases related to the chabazite-gmelinite family of zeolites have been synthesised,[4, 3] which contain only sodium as cation. It has become apparent therefore that a wide variety of compounds based on the chabazite-type of structure can be synthesised, in which the synthetic phases differ appreciably from their naturally occurring analogues. In the present paper an account will be given of the reactions and reactivity of various cation-exchanged forms of a natural rather siliceous chabazite, as revealed by differential thermal analysis, thermogravimetry, and *X*-ray diffraction. In later papers, a similar study of the synthetic potassium chabazite-like phases will be given, and of the hydration of members of the chabazite–gmelinite group of zeolites.

X-Ray powder photography has been used by Milligan and Weiser [5] in a systematic study of dehydration and stability of zeolites and hydrous oxides. Zveshnikova and Kuznetsov [6] have investigated relations between kaolinites and certain fibrous zeolites, using differential thermal analysis, and Koizumi [7] and Koizumi and Kiriyama [8] have examined dehydration of a considerable number of zeolites by use of *X*-rays and differential thermal analysis. Koizumi reported that four groups of zeolites could thus be distinguished. From differential thermal analysis of natrolite, scolecite, and mesolite Peng [9] concluded that in certain of these zeolites the water molecules may be arranged in groups having different volatilities. Such a view accords with *X*-ray structure determinations for these species.[10]

EXPERIMENTAL

Apparatus.—The equipment for differential thermal analysis was based on that used by Mackenzie.[11] The three main sections (furnaces, recorder unit, and control unit) were connected by two cables, one carrying the power connections and the other the thermocouple

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[1] Barrer, *Trans. Brit. Cer. Soc.*, 1957, **56**, 155.
[2] Barrer and Baynham, *J.*, 1956, 2882, 2892.
[3] Barrer and Bultitude, unpublished work.
[4] Breck, Linde Air Products Co., personal communication
[5] Milligan and Weiser, *J. Phys. Chem.*, 1937, **41**, 1029.
[6] Zveshnikova and Kuznetsov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1946, 25.
[7] Koizumi, *Mineralog. J. (Mineralog. Soc. Japan)*, 1953, **1**, 36.
[8] Koizumi and Kiriyama, *J. Geol. Soc. (Japan)*, 1953, **59**, 88; Sci. Report No. 2, Osaka Univ., 1953.
[9] Peng, *Amer. Mineralog.*, 1955, **40**, 834.
[10] Taylor, Meek, and Jackson, *Z. Krist.*, 1933, **84**, 373.
[11] Mackenzie, *Anal. Edafol. Fisiol. Veg.*, 1952, **11**, 159.

circuits. Ceramic furnace blocks and covers and small double cells were used. The cells contained the inert comparison specimen (ignited kaolin) and the reactive specimen, as well as the hot junctions of two thermocouples. Before introducing the reactive specimens into the cell, they were ground to pass 200 mesh and equilibrated at $\sim$51% relative humidity by storage for $\nless$4 days in a desiccator over a saturated solution of calcium nitrate.* The two cavities in the double cell were completely filled each time with the reactive sample and ignited kaolinite respectively. If there was insufficient of the reactive sample to fill the appropriate half of the double cell, it was mixed with ignited kaolin. A small metal plunger was used to pack the materials tightly and to reproduce the packing density as accurately as possible. The procedure of using equal volumes of sample and of reference material in the two halves of the cell provided the most reproducible temperature distribution throughout the specimen holder and thus gave a base line in the thermogram with the minimum of drift.

The apparatus was designed to provide a heating rate of 10° per min. up to about 1100° c. Any one of four identical furnaces could be heated and the rate was governed by the programme controller from a thermocouple embedded in the furnace core. The temperature of the inert reference material was recorded on a two-point recorder and the differential temperature on one of two instruments, (i) a potentiometric microvolt recorder or (ii) a direct reading millivolt recorder. The recorder systems were enclosed in an air thermostat. Most of the construction of this apparatus is due to Dr. J. S. Raitt, and to the workshop of the Chemistry Department, Aberdeen University.

TABLE 1. *Exchanges in chabazite.*

Exchanger	Solution	Strength of soln. (%)	Method	Temp.	Exchange (%)
Natural chabazite	NaCl	20	Steam-bath	90°	100
,,	$CaCl_2$	20	,,	90	100
Ca-chabazite	LiCl	20	,,	90	100
,,	KCl	20	,,	90	100
,,	NH_4Cl	20	,,	90	95·5
Na-chabazite	$SrCl_2$	20	,,	90	79
,,	$BaCl_2$	20	,,	90	90
Natural chabazite	$PbCl_2$	20	,,	90	$\sim$45
Ca-chabazite	RbCl	10	Sealed tube	110	100
,,	CsCl	10	,,	110	89·7
Natural chabazite	$Cu(NO_3)_2$	1	,,	25	50·6

TABLE 2. *Analysis of some ion-exchanged chabazites.*

	Molar proportions of constituents						
Mineral	SiO_2	Al_2O_3	CaO	BaO	SrO	Na_2O	H_2O
Natural chabazite	5·00	1·00	0·87	—	—	0·17	6·75
Na-chabazite	5·05	1·00	—	—	—	1·00	5·99
Ca-chabazite	5·11	1·00	0·97	—	—	—	6·91
Sr-chabazite	5·12	1·00	—	—	0·79	0·21	6·64
Ba-chabazite	5·15	1·00	—	0·90	—	0·10	6·17

The thermogravimetric apparatus included a furnace for heating the specimen operated by the same programme controller as were the furnaces of the apparatus for differential thermal analysis, and identical with these furnaces. Thus the heating rate was again 10° per minute. The specimen was suspended in a bucket by a very fine platinum filament from one arm of a suitably modified Stanton Model A.42 air-damped aperiodic balance. The wire was protected from draughts; the balance was shielded from heat from the furnace by sloping baffles.

For X-ray examination an HRX X-ray unit was employed. Hilger 9 cm. powder cameras were available. A copper anode bombarded by 38—39 kv electrons produced Cu-K_α and Cu-K_β characteristic radiation from which the Cu-K_β radiation was removed by means of nickel filters. Filaments were run at 15—20 milliamp. each, and exposure times of 4—6 hr. then normally sufficed for producing a good X-ray powder photograph.

Materials.—Natural chabazite from the Bay of Fundy, Nova Scotia, was used as parent material. From it ion-exchange products rich in Li, Na, K, Rb, Cs, NH_4, Ca, Sr, Ba, Pb, and

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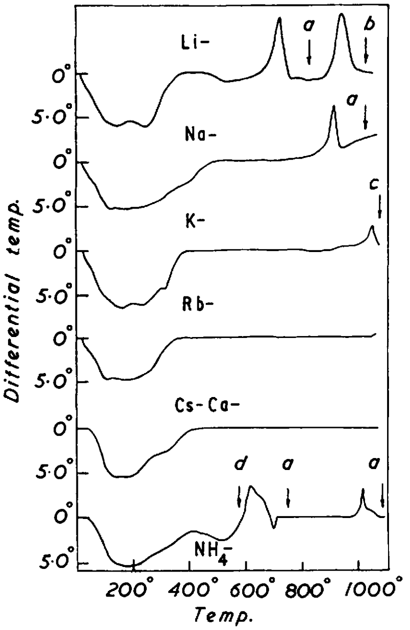
* The relative humidity of such solutions varies somewhat with ambient room temperature. However, in the small temperature interval involved this variation is small, and in this region the water sorption is moreover nearly independent of humidity, owing to the rectangular shape of the isotherms.

Cu were made. In all these preparations the aqueous chlorides were employed, except in the case of Cu-rich chabazite for which aqueous nitrate was the exchanging solution. Some details are summarised in Table 1, and full analyses of the original chabazite and of its Na, Ca, Sr, and Ba forms are in Table 2. In these analyses standard analytical procedures were employed.[12] The chabazite is seen to be rich in silica.

RESULTS

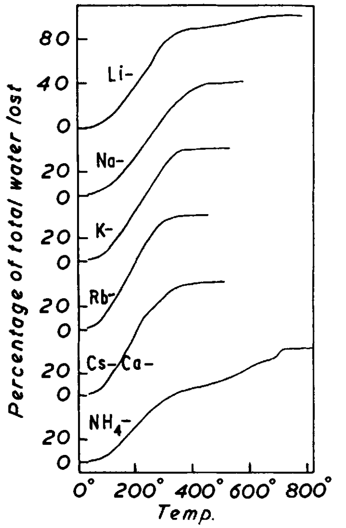
Thermograms and Thermogravimetric Curves.—The curves for differential thermal analysis of some of the ion-exchanged forms derived from natural chabazite are shown in Fig. 1. The major endotherm of Li-chabazite extends from room temperature to ~390°. It is followed by a second, small endotherm starting at ~445° and merging into the first exotherm at about 660°. The peak temperatures of the two strong exotherms are at 731° and 955° respectively. In the Na-chabazite thermogram the two endotherms for the Li-form are replaced by one extending to 510°, and there is only one exotherm with a peak temperature at 921°. The endotherm of K-chabazite is completed at 408°, and the exotherm is less pronounced and occurs at 1064°. Rb-chabazite, which even approaching 1100° shows only the beginning of an exothermic process, has an endotherm terminating by 386°.

FIG. 1. *Differential thermal analysis of ion-exchanged natural chabazites.*
($Al_2O_3 : SiO_2 = 1 : 5{\cdot}05$.)



a, Quartz; *b*, β-eucryptite; *c*, leucite; *d*, H-chabazite.

FIG. 2. *Thermogravimetric curves for ion-exchanged natural chabazites.*
($Al_2O_3 : SiO_2 = 1 : 5{\cdot}05$.)



The four samples above each contain only one type of exchangeable cation, but the Cs-rich crystals contain $Cs^+ : Ca^{2+}$ ions in the ratio 18 : 1 (Table 1). At 250° the slope of the endotherm starts decreasing, and there is a small " plateau " which is completed by 460°. This final part of the curve can reasonably be attributed to the presence of the Ca ions and the water associated with them. The Cs-rich form showed no exotherm up to ~1100°.

In order to demonstrate that the endothermic sections of the differential thermal analysis curves were associated with water loss, the thermogravimetric curves of Fig. 2 were determined.

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[12] *E.g.*, Harwood, " Practical Rock Analysis for Geologists," Imp. Coll. Science Technol., 1933; Vogel, " Quantitative Analysis," Longmans, London, 1948.

The first of these shows that water loss from Li-chabazite occurs in two stages, in agreement with the curve of Fig. 1. Fig. 2 shows also that completion of water loss has occurred at temperatures close to those at which the endothermal parts of the curves of Fig. 1 are completed.

The thermograms and thermogravimetric curves of Ca-, Sr-, and Ba-chabazite are shown in Figs. 3 and 4. The outstanding feature of Fig. 3 is the width of the endothermic parts. That for Ca-chabazite extends to 760° with a minimum at 220°. The corresponding thermogravimetric curve is smooth and slopes rather gently (Fig. 4). For Sr-chabazite, and particularly for Ba-chabazite, the water loss involves more than one stage. However, from Table 1 the numbers of ions present are respectively in the ratios Sr : Na = 79 : 42 and Ba : Na = 90 : 20. The sodium ions present may influence the differential thermal analysis and thermogravimetric curves. The endothermic section of the former curve of Ba-chabazite shows three parts, and the thermogravimetric curve shows that all are associated with some weight loss, so that the presence of sodium cannot explain the whole effect. The loss in weight in the last section of the endotherm is small and therefore it seems unlikely that the considerable heat effect can be due to water loss only.

FIG. 3.

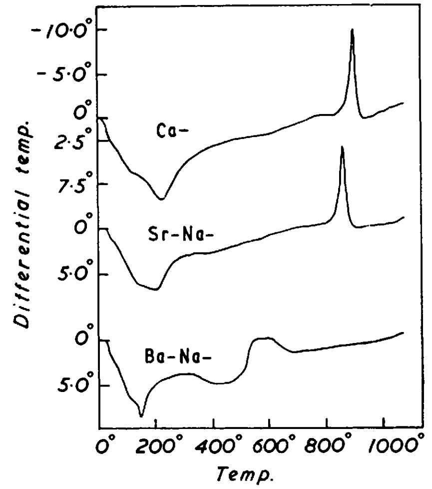
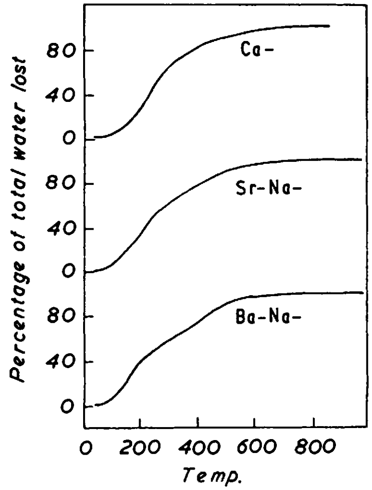


FIG. 4.



FIGS. 3 & 4. (Fig. 3) *Differential thermal analysis and* (Fig. 4) *thermogravimetric curves of natural chabazites rich in alkaline-earth metal ions.*

The differential thermal analysis curves for the chabazites enriched in copper and lead (Table 1) were also determined. Since some calcium and sodium were also present the curves are difficult to interpret and will not be considered further. There remain however the interesting curves for NH_4-chabazite (Figs. 1 and 2). Both are complex: in the endotherm water loss is also associated with loss of ammonia. There then follows an exothermic change with a peak at 614°, followed at once by a further endothermic process, giving a minimum at 692°. Finally, above 1000°, another exothermal reaction occurred. This thermogram is in some ways unique.

Structural Changes Associated with Differential Thermal Analysis.—*X*-Ray powder photographs were taken of the various ion-exchanged chabazites before and after heating to various temperatures in the furnaces of the differential thermal analysis apparatus. The heating rate was 10° per min., until the desired temperature was reached. Heating was then stopped and the material cooled rapidly in air. For temperatures below ~700° the powder was actually heated in very thin-walled Pyrex capillary tubes, which were quickly sealed after cooling. For temperatures above 700°, after the heat treatment the air-cooled powder was transferred as speedily as possible into the capillary tubes, which were again sealed. The *X*-ray powder photograph was then obtained. The maximum heating temperatures were at selected intervals between 20° and 1100°, these temperatures being chosen to follow changes revealed by the thermograms.

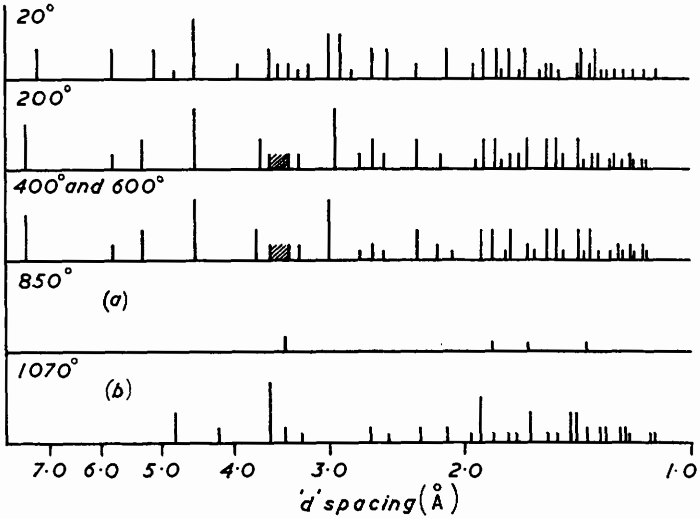


Fig. 5: Li-*chabazite.*

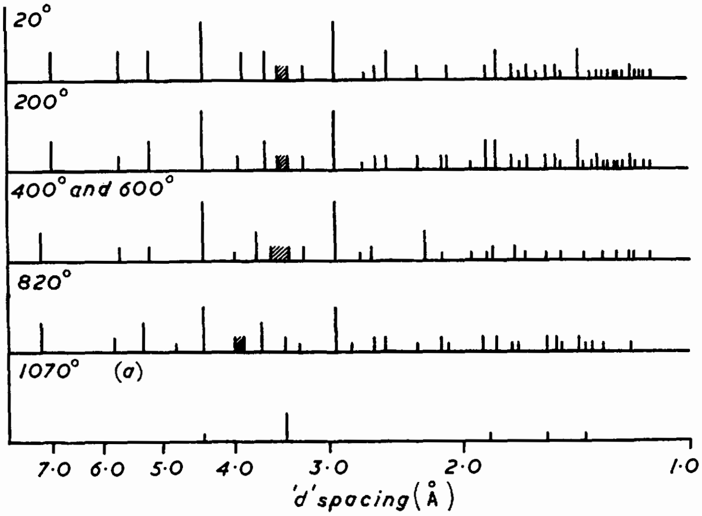


Fig. 6: Na-*chabazite.*

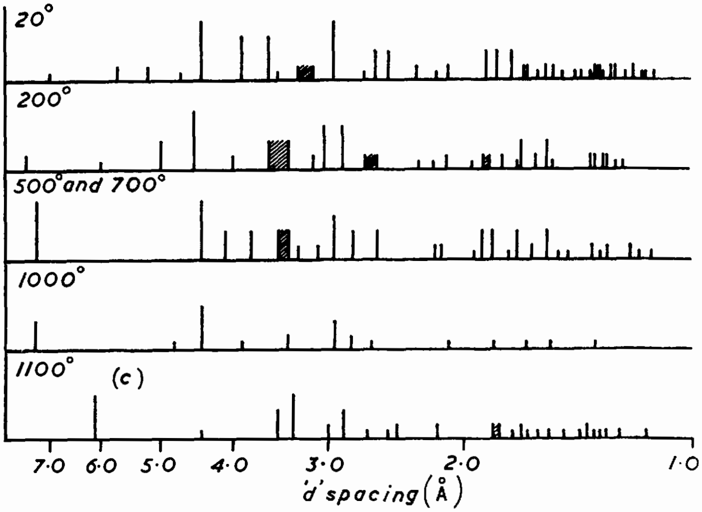


Fig. 7: K-*chabazite.*

The progressive changes in *X*-ray powder photographs following these heat treatments are illustrated in Fig. 5 (Li-chabazite), Fig. 6 (Na-chabazite), Fig. 7 (K-chabazite), Fig. 8 (NH_4-chabazite), and Fig. 9 (Ca-chabazite). These studies confirm that in many cases the basic structure of the chabazites remains unchanged both during, and for an interval after, water loss.

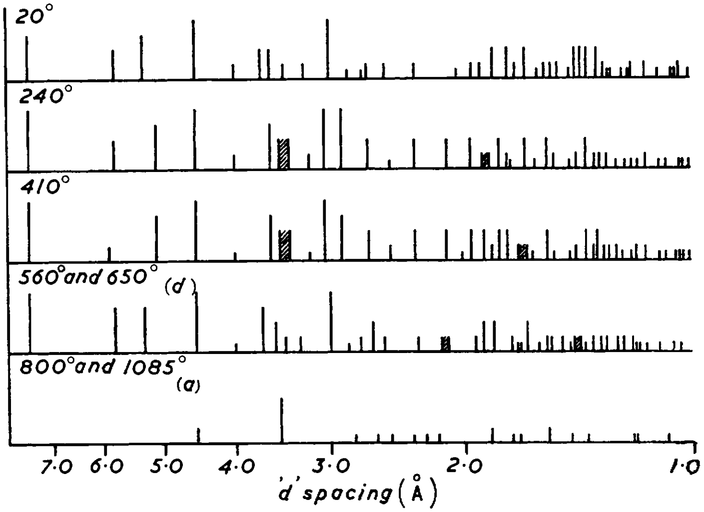


Fig. 8: NH_4-*chabazite.*

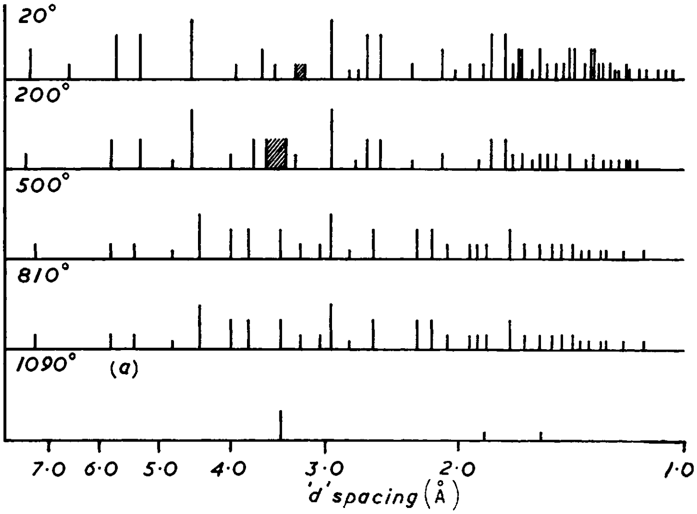


Fig. 9: Ca-*chabazite.*

FIGS. 5—9. *Lattice alterations with increasing temperature.*
a, Quartz. *b*, *β*-Eucryptite. *c*, Leucite. *d*, H-chabazite.

The patterns obtained for samples of Li-chabazite heated to 200°, 400°, and 600° are almost exactly identical, showing little evidence of alteration during dehydration of the crystals. After the first exotherm of this material (Fig. 1), *i.e.*, for the sample heated to 850°, the lattice was completely destroyed, and a weak quartz pattern appeared. After the second exotherm a strong β-eucryptite pattern was obtained.

The patterns of Na-chabazite heated to 200°, 400°, and 600° are identical in the low-angle diffractions but, between 200° and 400° where most of the water is lost, displacements of some of the weaker medium- and high-angle lines are observed. The 600° pattern is retained up to the temperature of the exothermic peak of the thermogram (Fig. 1), but by 1070° there is only a weak quartz pattern.

The *X*-ray powder photographs of specimens of K-chabazite, heated to various temperatures, show the same trend. The diffraction photograph for the 200° sample shows appreciable differences from that of the untreated sample, even among the strong lines at the low-angle end of the film. These shifts correspond to a small lattice contraction. Between 500° and 700° no reaction occurred, but at 1000° considerable lattice breakdown has taken place, while after the exothermic peak of Fig. 2, at 1090°, the product was amorphous. However, a further 12 hours' heating at 1100° resulted in recrystallisation to leucite.

Only one photograph was taken of Rb-chabazite, that of a sample heated to 1070° in a differential thermal analysis. This sample proved to have the same powder pattern as the original Rb-chabazite except for a weakening of the lines.

Similarly, the Cs-rich chabazite of Table 1 after being heated to 1060° remained identical with the parent structure.

Ca-chabazite showed much the same thermal stability as the potassium form. Between 200° and 500° the medium- and high-angle lines showed some displacement. Between 500° and 810° there was no further change, but at 1090° a weak quartz pattern appeared.

In Sr-chabazite similar changes were observed. Up to 300° there was little alteration; between 300° and 500° changes in some line positions and intensities were noted, but at 700° the pattern was still similar to that at 300°. Photographs of samples heated above 900° all gave weak quartz patterns.

The *X*-ray results for NH_4-chabazite are rather difficult to understand. Already at 240° there are some significant differences from the pattern of the original unheated crystals. There is then little change between 240° and 410°; but at 560° and at 650° (*i.e.*, at temperatures just before and just after the first exotherm in Fig. 2) the *same* pattern was found, which was close to that of a sample of H-chabazite previously prepared and *X*-rayed in these laboratories.[13] A sample heated to 800° or above showed a weak quartz pattern only, so that evidently reactions occurring between 560° and 650° are superseded by complete lattice breakdown.

DISCUSSION

The stability of the Li-, Na-, K-, Rb-, and Cs-rich forms of the chabazite shows an interesting gradation. Fig. 5 indicates how lattice breakdown is postponed to increasingly higher temperatures as the size of the cations increases. The Rb and Cs forms are indeed stable under the conditions of differential thermal analysis to 1000° or higher. This behaviour can be related to the capacity of the ions to fill space in the intracrystalline cavities in the chabazite lattice after the removal of zeolitic water by heat. The same behaviour has been observed with the Na, K, Rb, and Cs forms of analcite. While the Na form undergoes lattice breakdown when heated, the K, Rb, and Cs forms, which are anhydrous, remain stable to temperatures far above 1000°.[1,14] The smaller cavities in this zeolite are evidently filled by K (in leucite), Rb, and Cs without need for water molecules to saturate the intracrystalline volume. Such a degree of filling of the larger cavities in chabazite is not achieved, and there is room for additional water even when the lattice is very rich in cæsium. This may be the reason why, though cæsium evidently stabilises chabazite, it probably does not do so to the same extent as with analcite.

Consideration of the endotherms and corresponding weight-loss curves of differential thermal analysis has shown that sometimes (*e.g.*, for Li-, Sr-, and Ba-chabazite) the water is given up in more than one stage. This may be analogous to the situation described by Peng [9] for some fibrous zeolites. Peng considered that such stages indicated that water molecules in the zeolites are arranged in groups having different volatilities. However, there are other explanations. In the fibrous zeolites, where lattice rearrangements can occur rather easily on heating,[5] such rearrangements of themselves may change the environment of the water molecules remaining, and this in turn may alter the volatility of the remaining water. In the chabazite crystals which we have studied, the alumino-silicate framework is more robust and less prone to alteration than are those of the fibrous

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[13] Barrer and Sammon, *J.*, 1955, 2838.

[14] Barrer, Baynham, and McCallum, *J.*, 1953, 4035.

zeolites. The cations, however, are just as mobile, and are closely associated with intracrystalline water. When the amount of this water falls sufficiently, the positions of some or all of the cations may be rearranged, thus changing the water volatility.

One other feature of the endotherms and thermogravimetric curves may be indicated. The larger the cation in a series such as Li, Na, K, Rb, Cs, the lower tends to be the temperature at which substantially all the water is lost. This suggests a retentivity for water which is readily explained in terms of the association between cations and water dipoles. The binding energy from this source should be smaller for bigger ions. The bivalent ions, again as expected, show a greater retentivity than do univalent ions of comparable radius (Ca > Na and Ba > K).

The chabazites used in the present study are rather siliceous. Because of this it is not surprising that a common product of sintering was quartz, which was formed from Li-, Na-, NH_4-, Ca-, and Sr-chabazite. Other species produced were β-eucryptite (from Li-chabazite), leucite (from K-chabazite), and H-chabazite (from NH_4-chabazite). From the known compositions of these phases it is seen that disproportionation normally accompanies decomposition by sintering. Thus, for quartz formation:

$$(M_2,M)O,Al_2O_3,5SiO_2 \longrightarrow \underset{\text{(glass)}}{(M_2,M)O,Al_2O_3,(5-n)SiO_2} + \underset{\text{(quartz)}}{nSiO_2}$$

The other disproportionation product is represented in this equation as a glass, since no other diffraction pattern accompanied the appearance of the quartz lines. If the glass is the usual network structure with aluminium and silicon in tetrahedral co-ordination, n in the reaction equation should not exceed about three, if the validity of Lowenstein's rule is accepted.

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